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Some improved transition probabilities for neutral carbon

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Abstract

An earlier paper (Zatsarinny O and Froese Fischer C 2002 *J. Phys. B: At. Mol. Opt. Phys.* **35** 4669) presented oscillator strengths for transitions from the $2p^2$ 3P term to high-lying excited states of carbon. The emphasis was on the accurate prediction of energy levels relative to the ionization limit and allowed transition data from the ground state. The present paper reports some refined transition probability calculations for transitions from $2p^2\,{}^3P$, ${}^1D$, and ${}^1S$ to all odd levels up to $2p3d\,{}^3P^o$. Particular attention is given to intercombination lines where relativistic effects are most important.

1. Introduction

It has recently been observed [1] that the experimental transitions probabilities [2, 3] for lines in the $2p^2\,{}^3P$–$2p3d\,{}^3F^o$ multiplet in neutral carbon have ratios that differ widely from theoretical results reported earlier using a non-orthogonal B-spline frozen-cores R-matrix method [4]. The emphasis of the latter was on the accurate prediction of energy levels relative to the ionization limit for highly excited states and transition data for allowed transitions from $2p^2\,{}^3P$. Important for such a calculation were correlation and the relativistic shift, particularly for the interacting 2p*n*d and 2p*n*s Rydberg series. Not as important was the mixing of different LS terms in the LSJ Breit–Pauli approximation. In fact, the calculation [4] included only the spin–orbit operator in addition to the relativistic shift corrections. But there is no spin–orbit interaction between the configuration states $2p4s\,{}^3P^o_2$ and $2p3d\,{}^3F^o_2$, only spin–spin and spin–other-orbit and these might be important since the observed levels are only 50.98 cm^{-1} apart[1]. Interactions of the outer electrons with the $1s^2$ core were neglected.

Previous multiconfiguration Hartree–Fock (MCHF) calculations [6] for carbon did not include the 2p3d levels. In the present paper, these calculations have been repeated with

[1] The customary unit cm^{-1} used here is related to the SI units of energy (joules) by $1\ cm^{-1} = 1.986\,445\,61(34) \times 10^{-21}$ J [5].

somewhat larger wavefunction expansions and extended to include these levels. The new results are compared with the non-orthogonal B-spline R-matrix (BSR) results, previous MCHF data [6] and critically evaluated values [7]. The branching ratios for the $2p^2\ ^3P$–$2p3d\ ^3F^o$ multiplet are in better agreement with experiment.

2. Computational details

The theory and method are essentially the same as was described in previous work [6] except that expansions were over a larger set of configuration states and more levels were included, namely the levels of 2p3d and 2p4s. The same number of orbitals were used.

Wavefunction expansions were over sets of configuration state functions (CSF) from configurations $\{1\}\{1, 2\}^2\{2, 3, 4\}\{2, 3, ..6\}^2$ and $\{1\}^2\{2\}\{2, 3, 4\}\{2, 3, ..8\}^2$, where the notation $\{2, 3, ..8\}^2$, for example, indicates the set of all possible two-electron combinations over the indicated orbitals without regard to the orbital angular quantum number. From this set, those CSFs were selected that interacted with one or more members of the multi-reference set $1s^2\{2\}^3\{2, 3, 4\}$, namely the set of CSFs with a closed $1s^2$ core, three $n = 2$ electrons, and one nl electron with $n = 2, 3$ or 4. In the wavefunction expansions, orbital quantum numbers were restricted to $l = 4$ (g-electrons) whereas in the multi-reference set, the maximum was $l = 2$ (d-electrons).

Allowing for excitations from the 1s-subshell greatly increases the size of wavefunction expansions. After reducing LS expansions by eliminating all CSFs with a coefficient less than 0.000 01, the $^3P^o$ expansion included 20 222 CSFs. The correction to the wavefunction that results from an exciting one 1s electron and another outer electron of a CSF in the reference set accounts for the polarization of the core and is referred to as core-valence correlation.

The orbital optimization for the even $2p^2\ ^3P$, ^1D and $^1S_0$ terms was straightforward. A simultaneous optimization scheme was used for the lowest eigenstate of each LS term. The odd terms were divided into two groups for optimization. Group 1 included the more compact $2s2p^3\ ^3D^o$, $^3P^o$ and $^5S^o$ terms, along with $2p3s\ ^{1,3}P^o$. The radial functions of orbitals were optimized for these five terms, with 1s,2s,2p kept fixed after $n = 4$. The second group included the terms of 2p3d ($^{1,3}P^o$, $^{1,3}D^o$ and $^{1,3}F^o$) and 2p4s ($^{1,3}P^o$). The odd $2p3d\ ^{1,3}D^o$ and $^{1,3}P^o$ terms are not the lowest terms of their symmetry. By far the most difficult calculation is the one for the ^3P spectrum. The $2p3d\ ^3P^o$ is the fourth eigenstate of the $^3P^o$ manifold and interacts with $2p3d\ ^3F$ for $J = 2$ primarily through a spin–orbit interaction. Thus it is important to get an accurate energy separation of these levels. The $2p4s\ ^3P^o$ is the third eigenstate and needs to be orthogonal to $2p3s\ ^3P^o$ the lowest eigenstate. At the same time, it was found that the eigenstates were only in their proper order if $2s2p^3\ ^3P^o$ (the second eigenstate) was included in the optimization. For this reason, orbitals with $n \leqslant 6$ were obtained by optimizing only on the four lowest $^3P^o$ eigenstates. The optimization of the $n = 7, 8$ orbitals included the eigenstates of $2s2p^3$, 2p4s, $2p3d\ ^3P^o$, $2p3d\ ^3D^o$ and $2p3d\ ^3F^o$ with the $^3P^o$ eigenstates each having a weight of unity, $^3D^o$ a weight of two and $^3F^o$ a weight of five.

The above process results in three sets of orbitals, orthogonal within the set but non-orthogonal between sets. Each orbital set was then used in a Breit–Pauli configuration interaction calculation that included all the odd or even terms to determine the wavefunction expansion for the levels of the LS terms associated with the group. In theory, the wavefunctions for all the odd levels could have been obtained from one orbital set, but the energy levels of the first odd group were in slightly better agreement with observed when optimized separately.

Table 1 shows the observed energy levels and the differences between observation and theory. Because the fine-structure splitting is small, the differences are similar for all levels of a term. Consequently, only the difference for one level is reported. For the $2p^2\ ^3P_2$ level, the

Table 1. Comparison of energy levels (in cm^{-1}). Tabulated are the ASD [7] energies and the differences, E(theory)$-E$(ASD), for BSR [4], the MCHF+BP results without core-valence correlation (previous [6]) and present with core-valence correlation.

			Difference (theory−observations)		
Configuration	Level	Energy	BSR	Previous	Present
$2p^2$	$^3P_2$	43	5.54	−0.37	0.15
	$^1D_2$	10 193		76	123
	$^1S_0$	21 648		171	196
$2s2p^3$	$^5S^o_2$	33 735	123	−5	9
2p3s	$^3P^o_2$	60 738	151	345	22
	$^1P^o_1$	61 982	173	432	36
$2s2p^3$	$^3D^o_3$	65 386	1299	254	210
	$^3P^o_2$	75 255	1245	816	226
2p3d	$^1D^o_2$	77 680	50		105
2p4s	$^3P^o_2$	78 148	53		65
2p3d	$^3F^o_3$	78 216	36		77
	$^3D^o_3$	78 318	59		73
2p4s	$^1P^o_1$	78 340	52		75
2p3d	$^1F^o_3$	78 530	26		72
	$^1P_1$	78 731	44		75
	$^3P^o_2$	79 311	513		137

Table 2. Comparison of observed and theoretical level separation. The ratio of the theoretical difference relative to observed is given in parentheses.

	Energy		
Line	ASD	BSR	MCHF
2p4s $^1P^o_1$–2p3d $^3D^o_1$	46.79	39.07(0.84)	49.04(1.05)
2p3d $^3F^o_2$–2p4s $^3P^o_2$	50.98	33.36(0.65)	62.44(1.22)
2p3d $^3D^o_2$–2p3d $^3F^o_2$	108.56	132.78(1.22)	104.45(0.96)
2p3d $^3D^o_3$–2p3d $^3F^o_3$	102.75	125.75(1.22)	98.81(0.99)

difference has been improved significantly by including two-body operators in the Breit–Pauli calculation (included in the last two columns). The earlier MCHF calculations had expansions over the set of configuration states $\{1\}\{1, 2\}^2\{2, 3\}\{2, 3, \ldots, 6\}^2$ and $\{1\}^2\{2\}\{2, 3\}\{2, 3, \ldots 8\}^2$. This model assumes that components of the wavefunction containing $4l$ orbitals are small corrections. The present model allows for the possibility that CSFs containing $4l$ orbitals may be important components of the wavefunction, either from near-degeneracy effects or through the use of a common orbital basis. The resulting larger expansion accounts for the improvement in the present results over earlier MCHF calculations. The ground state total energy was lowered by 0.003 24 au, and if the total energies of higher levels are lowered by a lesser or greater amount, the levels shift in the spectrum where energies are relative to the total energy of the ground state. No improvement is observed in the $2p^2\ ^1D_2$ and $^1S_0$ energy levels, but most entries of the first odd group of levels have improved appreciably. The importance of the 4s,4p,4d orbitals is seen in the expansion for $2s2p^3\ ^3P^o_2$, namely

0.75	$2s2p^3$	+0.36	2p3d	+0.28	$2s2p^2(^3P)3p$	+0.28	2p4s
−0.18	2p4d	−0.16	$2s2p^2(^3P)4p$	+0.12	$2s2p^2(^1D)3p$	−0.12	2p3s

Table 3. Wavelength λ (in vacuum), line strength S, oscillator strength f and transition probability A_{ki} (in s^{-1}) for electric dipole (E1) transitions between all computed levels and forbidden (E2 and M1) transitions between the even levels. All transition probabilities are computed using the *ab initio* transition energies. The notation `x.xxe ± n` represents $x.xx \times 10^{\pm n}$.

Multiplet terms	g_i	g_k	Type	λ (Å)	S	f_{ik}	A_{ki} (s^{-1})
$2s^2\ 2p^2$–$2s^2\ 2p^2$							
$^3P\ ^3P$	1	5	E2	2 296 170	5.000e+00	6.934e−17	1.754e−14
	3	5	E2	3 700 145	1.125e+01	1.243e−17	3.633e−15
	1	3	M1	6 051 508	2.000e+00	1.336e−09	8.114e−08
	3	5	M1	3 700 145	2.500e+00	9.107e−10	2.662e−07
$^3P\ ^1D$	1	5	E2	9694	2.386e−05	4.397e−15	6.242e−08
	3	5	E2	9710	6.072e−05	3.712e−15	1.576e−07
	5	5	E2	9735	4.450e−04	1.620e−14	1.140e−06
	3	5	M1	9710	1.280e−05	1.777e−12	7.544e−05
	5	5	M1	9735	3.841e−05	3.190e−12	2.245e−04
$^3P\ ^1S$	5	1	E2	4587	4.080e−05	1.419e−14	2.250e−05
	3	1	M1	4581	8.489e−06	2.498e−12	2.381e−03
$2s^2\ 2p^2$–$2s2p^3$							
$^3P\ ^5S^o$	3	5	E1	2965	5.535e−07	1.890e−08	8.605e+00
	5	5	E1	2967	1.352e−06	2.768e−08	2.097e+01
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3s$							
$^3P\ ^3P^o$	1	3	E1	1656	7.805e−01	1.431e−01	1.160e+08
	3	1	E1	1657	7.795e−01	4.762e−02	3.470e+08
	3	3	E1	1657	5.839e−01	3.569e−02	8.672e+07
	3	5	E1	1656	9.779e−01	5.980e−02	8.731e+07
	5	3	E1	1658	9.746e−01	3.572e−02	1.445e+08
	5	5	E1	1656	2.925e+00	1.073e−01	2.608e+08
$^3P\ ^1P^o$	1	3	E1	1612	2.263e−04	4.263e−05	3.645e+04
	3	3	E1	1613	1.744e−04	1.095e−05	2.808e+04
	5	3	E1	1614	1.847e−04	6.955e−06	2.969e+04
$2s^2\ 2p^2$–$2s2p^3$							
$^3P\ ^3D$	1	3	E1	1555	3.680e−01	7.187e−02	6.607e+07
	3	3	E1	1556	2.755e−01	1.793e−02	4.943e+07
	3	5	E1	1556	8.277e−01	5.387e−02	8.910e+07
	5	3	E1	1556	1.831e−02	7.149e−04	3.281e+06
	5	5	E1	1556	2.751e−01	1.074e−02	2.958e+07
	5	7	E1	1556	1.544e+00	6.026e−02	1.185e+08
$^3P\ ^3P^o$	1	3	E1	1325	2.538e−01	5.818e−02	7.370e+07
	3	1	E1	1325	2.568e−01	1.962e−02	2.236e+08
	3	3	E1	1325	1.931e−01	1.476e−02	5.605e+07
	3	5	E1	1325	3.122e−01	2.386e−02	5.437e+07
	5	3	E1	1326	3.199e−01	1.466e−02	9.276e+07
	5	5	E1	1326	9.536e−01	4.370e−02	1.659e+08
	5	5	E1	1286	3.506e−04	1.656e−05	6.676e+04
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 4s$							
$^3P\ ^3P^o$	1	3	E1	1279	1.102e−01	2.617e−02	3.556e+07
	3	1	E1	1280	9.142e−02	7.234e−03	8.842e+07
	3	3	E1	1279	5.826e−02	4.611e−03	1.879e+07
	3	5	E1	1279	1.774e−01	1.404e−02	3.437e+07
	5	3	E1	1280	1.126e−01	5.347e−03	3.629e+07
	5	5	E1	1279	3.304e−01	1.569e−02	6.395e+07

Table 3. (Continued.)

Multiplet terms	g_i	g_k	Type	λ (Å)	S	f_{ik}	A_{ki} (s^{-1})
$^3P\ ^1P^o$	1	3	E1	1275	1.552e−02	3.696e−03	5.054e+06
	3	3	E1	1276	2.890e−02	2.294e−03	9.405e+06
	5	3	E1	1276	5.593e−03	2.663e−04	1.818e+06
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3d$							
$^3P\ ^1D^o$	3	5	E1	1286	7.836e−04	6.170e−05	1.494e+05
$^3P\ ^3F^o$	3	5	E1	1278	2.082e−02	1.650e−03	4.044e+06
	5	5	E1	1278	1.160e−02	5.511e−04	2.250e+06
	5	7	E1	1278	8.196e−02	3.896e−03	1.137e+07
$^3P\ ^3D^o$	1	3	E1	1276	3.879e−01	9.233e−02	1.261e+08
	3	3	E1	1276	2.852e−01	2.263e−02	9.265e+07
	3	5	E1	1276	8.729e−01	6.926e−02	1.702e+08
	5	3	E1	1277	1.835e−02	8.730e−04	5.953e+06
	5	5	E1	1277	3.243e−01	1.543e−02	6.317e+07
	5	7	E1	1277	1.639e+00	7.799e−02	2.281e+08
$^3P\ ^1F^o$	5	7	E1	1273	8.603e−03	4.106e−04	1.207e+06
$^3P\ ^1P^o$	1	3	E1	1269	1.376e−03	3.293e−04	4.547e+05
	3	3	E1	1269	6.502e−04	5.187e−05	2.148e+05
	5	3	E1	1270	1.283e−05	6.140e−07	4.235e+03
$^3P\ ^3P^o$	1	3	E1	1259	1.691e−01	4.080e−02	5.728e+07
	3	1	E1	1259	1.793e−01	1.443e−02	1.822e+08
	3	3	E1	1259	1.388e−01	1.116e−02	4.699e+07
	3	5	E1	1259	1.979e−01	1.591e−02	4.018e+07
	5	3	E1	1259	2.232e−01	1.077e−02	7.550e+07
	5	5	E1	1259	6.652e−01	3.209e−02	1.350e+08
$2s^2\ 2p^2$–$2s2p^3$							
$^1D\ ^5S^o$	5	5	E1	4268	4.813e−11	6.851e−13	2.508e−04
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3s$							
$^1D\ ^3P$	5	3	E1	1998	9.654e−04	2.936e−05	8.179e+04
	5	5	E1	1996	1.503e−05	4.575e−07	7.659e+02
$^1D\ ^1P^o$	5	3	E1	1934	3.616e+00	1.136e−01	3.375e+08
$2s^2\ 2p^2$–$2s2p^3$							
$^1D\ ^3D$	5	3	E1	1852	3.766e−07	1.235e−08	4.002e+01
	5	5	E1	1852	5.862e−07	1.923e−08	3.737e+01
	5	7	E1	1852	6.600e−06	2.164e−07	3.005e+02
$^1D\ ^3P^o$	5	3	E1	1535	8.587e−08	3.400e−09	1.605e+01
	5	5	E1	1535	7.148e−06	2.830e−07	8.016e+02
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 4s$							
$^1D\ ^3P^o$	5	3	E1	1473	3.680e−03	1.517e−04	7.770e+05
	5	5	E1	1473	1.772e−04	7.309e−06	2.248e+04
$^1D\ ^1P^o$	5	3	E1	1468	2.569e−01	1.063e−02	5.479e+07
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3d$							
$^1D\ ^1D^o$	5	5	E1	1482	2.770e−01	1.135e−02	3.447e+07
$^1D\ ^3F^o$	5	5	E1	1471	4.216e−04	1.741e−05	5.362e+04
	5	7	E1	1471	1.552e−02	6.408e−04	1.411e+06
$^1D\ ^3D^o$	5	3	E1	1469	1.127e−02	4.658e−04	2.398e+06
	5	5	E1	1469	7.359e−05	3.043e−06	9.404e+03
	5	7	E1	1469	5.347e−03	2.211e−04	4.883e+05

Table 3. (Continued.)

Multiplet terms	g_i	g_k	Type	λ (Å)	S	f_{ik}	A_{ki} (s^{-1})
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3d$							
$^1D\ ^1F^o$	5	7	E1	1464	1.935e+00	8.028e−02	1.784e+08
$^1D\ ^1P^o$	5	3	E1	1460	2.507e−01	1.043e−02	5.439e+07
$^1D\ ^3P^o$	5	3	E1	1446	2.654e−06	1.115e−07	5.925e+02
	5	5	E1	1447	3.086e−05	1.296e−06	4.132e+03
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3s$							
$^1S\ ^3P^o$	1	3	E1	2595	1.481e−04	1.733e−05	5.720e+03
$^1S\ ^1P^o$	1	3	E1	2489	6.312e−01	7.703e−02	2.764e+07
$2s^2\ 2p^2$–$2s2p^3$							
$^1S\ ^3D$	1	3	E1	2355	1.410e−07	1.819e−08	7.289e+00
$2s^2\ 2p^2$–$2s2p^3$							
$^1S\ ^3P^o$	1	3	E1	1864	2.714e−06	4.421e−07	2.828e+02
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 4s$							
$^1S\ ^3P^o$	1	3	E1	1775	8.801e−05	1.506e−05	1.063e+04
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 3d$							
$^1S\ ^3D^o$	1	3	E1	1769	6.328e−03	1.087e−03	7.718e+05
$2s^2\ 2p^2$–$2s^2\ 2p(^2P)\ 4s$							
$^1S\ ^1P^o$	1	3	E1	1768	1.985e−02	3.412e−03	2.428e+06
$2s^22p^2 - 2s^22p(^2P)\ 3d$							
$^1S\ ^1P^o$	1	3	E1	1756	6.673e−01	1.155e−01	8.329e+07
$^1S\ ^3P^o$	1	3	E1	1736	1.184e−04	2.072e−05	1.529e+04

All components are $^3P^o_2$. The 2p3s and 2p4s components arise from the interactions with nearby configuration states, but the others illustrate the flexibility needed to represent a set of wavefunctions in a common, orthogonal orbital basis.

For the upper odd levels, BSR appears to be the more accurate except for the fact that the differences for the present values are more constant and represent a shift of the spectrum. The Breit–Pauli interactions between different LS terms depend critically on the separation between levels. Table 2 shows the energy separation of levels with the same J of some closely space levels. Also tabulated are the BSR and present MCHF separations with the ratio of separations (theory/observed) in parentheses. In all cases, the present energies have better separation and ratios closer to unity. Thus, in those cases where the mixing of LS terms in the wavefunction composition is important, the present results can be expected to be more accurate. Examples are spin-changing transitions and the $2p^2\ ^3P$–$2p3d\ ^3F^o$ transition.

3. Transition probabilities

Table 3 reports transition probability data for all electric dipole (E1) transitions between the even and odd levels as well as the forbidden (E2 and M1) transitions within the even levels. More complete information that includes the length and velocity values for E1 and E2 transitions is available at the MCHF/MCDHF (Multiconfiguration Dirac–Hartree–Fock) website [8]. All quantities were calculated using *ab initio* transition energies.

Table 4 compares BSR [4], previous MCHF [6] and present MCHF transition probabilities, along with the ASD recommended values along with their accuracy ratings [7] for a number of i transitions. The $2p^2\ ^3P$–$2s2p^3\ ^5S^o$ transition arises through relativistic effects that are better described in the MCHF results. For a number of transitions, such as $2p^2\ ^3P$–$2p3s\ ^3P^o$

Table 4. Comparison of BSR [4] and MCHF+BP transition probabilities A_{ki} with critically evaluated Atomic Spectra Database (ASD) transition data and their accuracy [7] from theoretical sources [9]. MCHF results are computed using *ab initio* transition energies.

Transition	g_i	g_k	BSR	Previous	Present	ASD
$2p^2\ ^3P$–$2s2p^3\ ^5S^o$	3	5	7.20	8.48	8.61	
	5	5	2.17e+1	2.06e+1	2.10e+1	
$2p^2\ ^3P$–$2p3s\ ^3P^o$	1	3	1.07e+8	1.20e+8	1.16e+8	1.13e+8 A
	3	1	3.20e+8	3.60e+8	3.47e+8	3.43e+8 A
	3	3	8.01e+7	9.00e+7	8.67e+7	8.64e+7 A
	3	5	8.05e+7	9.06e+7	8.73e+7	8.58e+7 A
	5	3	1.33e+8	1.50e+8	1.44e+8	1.44e+8 A
	5	5	2.41e+8	2.71e+8	2.61e+8	2.52e+8 A
$2p^2\ ^3P$–$2p3s\ ^1P^o$	1	3	3.79e+4	3.50e+4	3.64e+4	3.01e+4 C+
	3	3	2.62e+4	2.60e+4	2.81e+4	2.21e+4 C+
	5	3	4.40e+4	2.66e+4	2.974+4	2.64e+4 C+
$2p^2\ ^3P$–$2s2p^3\ ^3D^o$	1	3	6.37e+7	7.07e+7	6.61e+7	6.57e+7 A
	3	3	4.76e+7	5.30e+7	4.94e+7	4.92e+7 A
	3	5	8.59e+7	9.54e+7	8.91e+7	8.86e+7 A
	5	3	3.14e+6	3.52e+6	3.26e+6	3.26e+6 A
	5	5	2.84e+7	3.17e+7	2.90e+7	2.94e+7 A
	5	7	1.41e+8	1.22e+8	1.18e+8	1.18e+8 A
$2p^2\ ^3P$–$2s2p^3\ ^3P^o$	1	3	6.00e+7	9.54e+7	7.37e+7	7.95e+7 B
	3	1	1.85e+8	2.87e+8	2.24e+8	2.41e+8 B
	3	3	4.63e+7	7.22e+7	5.60e+7	6.04e+7 B
	3	5	4.34e+7	7.09e+7	5.44e+7	5.89e+7 B
	5	3	7.57e+7	1.19e+8	9.28e+7	1.00e+8 B
	5	5	1.35e+8	2.14e+8	1.66e+8	1.79e+8 B

Table 5. Comparison of BSR [4] and MCHF transition probabilities A_{ki} (in units of 10^7 s^{-1}) with critically evaluated Atomic Spectra Database (ASD) transition data and their accuracy [7] from theoretical sources [9]. MCHF results are computed using *ab initio* transition energies.

		$2p^2\ ^3P$–$2p4s\ ^3P^o$			$2p^2\ ^3P$–$2p3d\ ^3P^o$		
g_i	g_k	BSR	Present	ASD	BSR	Present	ASD
1	3	3.57	3.56	3.11 B	7.23	5.73	5.32 B+
3	1	8.61	8.84	8.22 B	22.4	18.2	17.0 B+
3	3	1.79	1.87	1.73 B	5.75	4.70	4.42 B+
3	5	3.50	3.44	3.08 B	5.19	4.02	3.71 B+
5	3	3.54	3.63	3.33 B	9.31	7.55	7.06 B+
5	5	6.21	6.40	5.77 B	16.7	13.5	12.7 B+

and $2p^2\ ^3P$–$2s2p^3\ ^3D^o$, present results are in better agreement with the ASD compilations. The latter are based on results obtained by Hibbert *et al* [9] that include semi-empirical diagonal energy shifts by LS configuration in the interaction matrix in the determination of the wavefunctions. For both the $^3D^o$ and $^3P^o$ terms, $2s2p^3$ interacts strongly with one or more Rydberg series—2p*n*d in the case of the former and 2p*n*s and 2p*n*d in the case of the latter. In C I, the $2s2p^3\ ^3D^o$ Hartree–Fock energy is below all Hartree–Fock 2p*n*d energies, whereas $2s2p^3\ ^3P^o$ has an energy between the 2p3d and 2p4d and between 2p4s and 2p5s Hartree–Fock energies. Correlation is needed to lower the $2s2p^3$ terms to their observed positions. The semi-empirical corrections employed by Hibbert *et al* [9] appear to have done this effectively

Table 6. Comparison of BSR [4], CIV3 [9] and present transition probabilities A_{ki} (in s^{-1}) with critically evaluated ASD values [7] and their accuracy, based on experimental data [2, 3] for the $2p^2\ ^3P$–$2p3d\ ^3F^o$ transition. BSR and present results were computed using *ab initio* transition energies.

g_i	g_k	BSR	CIV3	Present	ASD
3	5	1.73e+6	3.15e+6	4.04e+6	1.80e+6 C
5	5	1.86e+6	1.86e+6	2.25e+6	8.10e+5 D+
5	7	6.24e+6	9.28e+6	1.13e+7	1.10e+7 C

Table 7. Comparison of FFS (Froese Fischer and Saha, 1985 [10]), CIV3 (Hibbert *et al* 1993 [9]), and present forbidden E2 and M1 transition probabilities. Present results are computed using *ab initio* transition energies.

		A_{ki}(E2)			A_{ki}(M1)		
g_i	g_k	FFS	CIV3	Present	FFS	CIV3	Present
$2p^2\ ^3P$–$2p^2\ ^3P$							
1	5	1.61e−14	1.72e−14	1.75e−14			
1	3				7.30e−8	7.96e−8	8.11e−8
3	5	3.29e−14	3.60e−15	3.63e−15	2.34e−7	2.67e−7	2.66e−7
$2p^2\ ^3P$–$2p^2\ ^1D$							
1	5	1.16e−7	8.34e−8	6.24e−8			
3	5	1.57e−7	8.21e−8	1.58e−7	7.45e−5	6.17e−5	7.54e−5
5	5	1.48e−6	1.05e−6	1.14e−6	2.22e−4	1.836e−4	2.24e−4
$2p^2\ ^3P$–$2p^2\ ^1S$							
3	1				2.24e−3	2.11e−3	2.38e−3
5	1	1.82e−5	1.93e−5	2.24e−5			
$2p^2\ ^1D$–$2p^2\ ^1S$							
5	1	5.67e−1	6.38e−1	6.19e−1			

in a number of cases ($2p^2\ ^3P$–$2s2p^3\ ^3D^o$ and $2p^2\ ^3P$–$2p3s\ ^3P^o$, for example). In other cases, present results agree most closely with the previous calculations.

Because of difficulties associated with perturbers, BSR results were restricted to 2p*n*s, $n \geqslant 4$ and 2p*n*d, $n \geqslant 3$. In table 5, BSR results for transitions from $2p^2\ ^3P$ to $2p4s\ ^3P^o$ and $2p3d\ ^3P^o$ are compared with present MCHF and ASD recommended values. There is excellent agreement between BSR and present MCHF for transitions to the former multiplet but better agreement between MCHF and ASD for the latter.

Of special interest in this paper are the transition probabilities for lines in the $2p^2\ ^3P$–$2p3d\ ^3F^o$ multiplet reported in table 6. These E1 transitions arise from the mixed composition of the $^3F^o_J$ wavefunction. In the present work, the expansion coefficients and CSFs of the leading components of the wavefunction are

$$^3F^o_2 : 0.952\,2p3d\,^3F^o + 0.198\,2p^3 3d\,^3F^o - 0.154\,2p3d\,^3D$$
$$^3F^o_3 : 0.939\,2p3d\,^3F^o + 0.196\,2p^3 3d\,^3F^o - 0.209\,2p3d\,^3D + 0.087\,2p3d\,^1F^o$$

The initial state is largely pure ^3P and so it is the $^3D^o$ component of the wavefunction that contributes to the transition rate for this transition. Table 2 showed that the $^3F^o$ and $^3D^o$ separation was accurately predicted in the present work which implies a good $^3D^o$:$^3F^o$

composition for the wavefunction. In table 6 theoretical values are compared with some experimental results. The CIV3 and present transition rates for the $^3P_2$–$^3F^o_3$ line agree well with each other and experiment, though there is considerable variation in the $^3P_{1,2}$–$^3F^o_2$ lines. These have the same upper state with only the initial state varying. In such cases, the ratio $A(^3P_1 - {}^3F^o_2)/A(^3P_2 - {}^3F^o_2)$, should be essentially constant regardless of the magnitude of the mixing. The theoretical ratios are 0.93, 1.7, 1.8 for BSR, CIV3 and present, respectively, compared with 2.2 for data derived from experiment. It is not clear why the non-orthogonal spline ratios are so different.

Finally, in table 7 we compare the forbidden E2 and M1 transition probabilities for transitions between the levels of the $2p^2$ configuration. Hibbert *et al* [9] used an effective spin–orbit operator selected to reproduce the 2p3s fine structure. This could limit the accuracy of these forbidden transitions. Generally, there is good agreement with the CIV3 values and present work, but for $2p^2\ ^3P$–$2p^2\ ^1D$ M1 transitions, there is better agreement with the MCHF+Breit–Paul results reported in 1985 [10].

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